a bridged activated complex of the kind which has been so successfully applied[29,30] to many charge-transfer exchange reactions.

Our experiences in preparing Na_2IrCl_6 and Na_3IrCl_6 unequivocally isotopically labeled with radioiridium suggest that care is necessary in preparing labeled complexes which undergo substitution reactions slowly. It does not appear safe to assume that a labeled complex at tracer concentrations will necessarily be in the same chemical form as the isotopic carrier with which it may be mixed, even though both have been through the same chemical treatment. Aquation and other reactions may take place at different rates and even to different equilibrium states for the tracer and carrier. Where certainty of labeling is to be ensured, the direct production of the desired radioactivity in a matrix of the metal (or elemental form where possible) at the appropriate specific activity has much to recommend it. Conversion of the labeled substance to the desired form without admixture with inactive isotopic substances and on a scale large enough to permit analytical characterization of the final product then results in a clearly labeled product.

Acknowledgment.—The authors wish to thank Dr. M. E. Remley and the operating staff of the North American Aviation, Inc., water boiler neutron source for irradiating the metallic iridium used for tracer F.

LOS ANGELES, CALIFORNIA

(29) H. Taube, H. Myers and R. L. Rich, THIS JOURNAL, **75**, 4118 (1953).

(30) H. Taube and H. Myers, *ibid.*, **76**, 2103 (1954).

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Heat of Combustion of Gadolinium[1,2]

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Calorimetric combustions of gadolinium metal were performed at an initial temperature of 24.6° under an oxygen pressure of 25 atm. The energy of combustion under these conditions was found to be 5773 ± 12 joules/g. The corresponding standard heat of formation of the sesquioxide (B-type) from the elements is calculated to be -1815.6 ± 3.6 kjoules/mole. No literature values are available for comparison.

Introduction.—Only recently have some of the rare earth metals become available in a sufficiently pure state for the determination of their chemical and physical properties. This paper reports the results of the combustion of analyzed gadolinium metal to determine the heat of formation of its oxide. No literature values are available for comparison.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in a bomb calorimeter at a known initial pressure of oxygen. The energy equivalent of the calorimeter was determined from the heat of combustion of benzoic acid and also was determined electrically. The completeness of combustion was determined by treating the combustion products with 8 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present.

The uncertainties given are twice the standard deviations.

The units of energy used are the absolute joule and the defined calorie; 1 defined calorie = 4.1840 absolute joules.

The unit of mass is the gram mass *in vacuo*. The gadolinium metal was weighed to the nearest 0.0001 g. The water for the calorimeter was weighed to the nearest 0.01 g.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[3] The bomb used in this work is the same as there described. Its volume is approximately 360 ml. The two methods of calibration gave substantial agreement. By the electrical method, carried out in 1950, the energy equivalent of the calorimeter filled with oxygen to 25 atm., based on 15 runs, was 10,092.4 ± 5.3 absolute joules/° where the uncertainty includes the uncertainty in the measuring instruments as well as the uncertainty due to random errors. Since that time the calorimeter has been calibrated periodically with benzoic acid (NBS standard samples 39f and 39g). There has been some slight variation in the values obtained although they are in agreement when the uncertainties attached to them are taken into consideration. The latest value, based on 20 runs using NBS sample 39g, is 10,099.8 ± 3.4 joules/° and is the value used in the work reported here.

Gadolinium Metal.—The gadolinium metal was supplied by Dr. F. H. Spedding of the Ames Laboratory of the A.E.C. This metal was analyzed at the Los Alamos Scientific Laboratory with the following results: Ca, 0.008%; C, 0.020%; N, 0.018%; O, 0.245%; and H, 0.021%. Any other metallic impurities were present in amounts too small to be detected by the spectroscopic method used. No other rare earths were found on examination of an aqueous solution by absorption spectra, the limits of detection being: Nd, 0.01%; Pr, 0.03%; Sm, 1.0%; Dy, 0.4%; Er, 0.04%. Excluding other rare earths the gadolinium thus contained about 0.31% impurities. The chemical state of the impurities is unknown. If it is assumed that the oxygen, nitrogen, hydrogen and carbon are combined with gadolinium as Gd_2O_3, GdN, GdH_2 and GdC_2, respectively, and not combined with the calcium, then the material is 97.05 mole per cent. gadolinium metal. A Debye X-ray pattern of the metal showed only lines of the metal in the hexagonal form.

Combustion of Gadolinium.—The gadolinium was burned as chunks on sintered discs of 90% gadolinium oxide supported on a platinum platform weighing 103.8 g. A piece of the metal showed no increase in weight after $1^1/_2$ hours in oxygen at 25 atm. The impurities in the discs consisted mainly of dysprosium and samarium oxides. New discs were used for each run. The discs were made by mixing 0.5% dextrin in water with the powder and pressing in a steel die at 10,000 p.s.i. They were fired in air for eight hours at 1150°. The oxygen used analyzed better than 99.5% O_2 with no detectable nitrogen. Pure magnesium was used for the fuse wire. Its heat of combustion was taken as 24,667 joules/g.[3] The amount varied from 0.0048 to 0.0054 g. The amount of magnesium is believed to be too small to account for any significant heat change, assuming that a double oxide was formed from magnesium and gadolinium oxides. Correction was made for the electrical energy used in igniting the wire. The total energy equivalent of the calorimeter and contents was used, taking into account the discs, the platinum and the difference in energy

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(1) This work was performed under the auspices of the A.E.C.

(2) Presented before the Section on Physical and Inorganic Chemistry, 126th Meeting, A.C.S., New York, N. Y., September 16, 1954.

(3) C. E. Holley, Jr., and E. J. Huber, Jr., THIS JOURNAL, **73**, 5577 (1951).

equivalent between the gadolinium oxide formed and the oxygen used.[4] Combustion was complete within the limits of the analysis. The initial temperature was 24.6° and the average final temperature was 25.8°. The results of the 7 runs are listed in Table I.

TABLE I

THE HEAT OF COMBUSTION OF GADOLINIUM

Run	Mass Gd burned, g.	Wt. Gd_2O_3, g.	Wt. Mg, g.	Joules/deg. Total	ΔT, °K.	Energy, total	Energy from— Firing, j.	Mg, j.	Gd, j.	Gd, j./g.	Dev. from mean j./g.
1	2.2001	43.7	0.00544	10126.3	1.2438	12595.1	19.2	134.4	12441.5	5655.0	16.3
2	2.0387	44.0	.00514	10126.3	1.1542	11687.8	9.0	127.0	11551.8	5666.3	5.0
3	2.3345	48.5	.00526	10127.6	1.3204	13372.5	11.0	130.0	13231.5	5667.8	3.5
4	2.0687	45.4	.0050	10126.6	1.1692	11840.0	12.2	123.5	11704.3	5657.8	13.5
5	2.2077	45.9	.00501	10126.9	1.2521	12679.9	10.1	123.8	12546.0	5682.8	11.5
6	2.2771	49.6	.00484	10127.9	1.2933	13098.4	8.7	119.6	12970.1	5695.9	24.6
7	2.1713	48.8	.0049	10127.7	1.2294	12451.0	11.4	121.1	12318.5	5673.3	2.0
							Standard dev. 5.4		Ave.	5671.3	10.9

This average value of 5671.3 ± 10.8 must be corrected for the impurities present.

Correction for Impurities.—If it is assumed that the oxygen is present as Gd_2O_3, the nitrogen as GdN which burns to Gd_2O_3 and NO_2, the carbon as graphite and the hydrogen as GdH_2, the percentage composition of the metal by weight is Gd metal, 96.25; Gd_2O_3, 1.85; GdN, 0.22; GdH_2, 1.66; C, 0.02; Ca, 0.008. The carbon is probably present as GdC_2, but the heat of formation of the latter is not known and is probably small. Since the amount of carbon is small, the error thus introduced is small. The calcium is assumed to contribute according to its heat of combustion in the pure state. Heats of alloy formation and heats of solution are ignored. If we let Q be the heat of combustion of pure gadolinium metal, per gram, then we may write the following equation: $0.9625Q + 3280 \times 0.0022 + 0.0002 \times 33{,}000 + 0.00008 \times 16{,}000 + 5980 \times 0.0166 = 5671.3$ joules/g. where the first term is the heat from the Gd metal, the second term is from the GdN, 3280 being the heat of combustion per gram of GdN to Gd_2O_3 and NO_2,[5] the third term is from the C, the fourth term from the Ca and the fifth term from the GdH_2, 5980 being the heat of combustion of GdH_2, per gram, to Gd_2O_3 and H_2O.[6] The sum of these terms is equated to the observed heat of combustion per gram. Solving, $Q = 5773.4$ joules/g.

If an alternative assumption is made that the calcium is present as the oxide with the extra oxygen present as Gd_2O_3, a value of 5773.5 is found. The average of these two values can be rounded off to 5773 joules/g. The correction due to impurities amounts to 1.80% of the uncorrected value.

Calculation of the Uncertainty.—The uncertainty to be attached to the corrected value includes the uncertainty in the energy equivalent which is 0.03%, the uncertainty in the calorimetric measurements which is 10.8 joules/g. or 0.19%, and the uncertainty introduced in the correction for impurities.

The main uncertainty introduced in the correction for the impurities is the accuracy of the analyses. The O, N, H and C were determined chemically with a possible error of 2% for the O, 30% for the N, and 5% for the H and C. The Ca was determined spectroscopically and it is estimated that it is correct to 50%. If the amounts of impurities are increased by the above-mentioned percentages and Q recalculated, the value 5776 joules/g. is obtained. On this basis, then, the uncertainty introduced in the correction is taken as the difference between 5773 and 5776 or 3 joules/g. which is 0.05%. There are additional small uncertainties not taken account of which have been discussed above.

Combining these uncertainties, the over-all uncertainty $= \sqrt{0.03^2 + 0.19^2 + 0.05^2} = 0.20\% = 11.5$ joules/g. And the final corrected value is 5773 ± 12 joules/g. for the heat of combustion of gadolinium metal in oxygen at 25 atm. pressure.

Composition of the Gadolinium Oxide.—The gadolinium oxide formed was tan in color. An X-ray pattern showed only lines of B type Gd_2O_3. Analysis by the method of Barthauer and Pearce[7] showed no oxygen above that necessary for the sesquioxide.

Heat of Formation of Gd_2O_3.—The heat of combustion reported above gives for the reaction in the bomb a value of $\Delta E_{24.6°} = -1811.6 \pm 3.6$ kjoules/mole (atomic weight Gd = 156.9). The correction of this value to 25° is less than the uncertainty in the result. To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. Using Rossini and Frandsen's[8] value of $(\partial \Delta E/\partial P)_{301°K.} = -6.51$ joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$, we have for the heat of formation of Gd_2O_3, (B-type), $\Delta H_{25°} = -1815.6 \pm 3.6$ kjoules/mole. In defined calories this is -433.94 ± 0.86 kcal./mole.

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[4] The specific heat of Gd_2O_3 is estimated at 0.27 joule/g./°.

[5] The heat of formation of GdN is estimated at −75 kcal./mole.

[6] The heat of formation of GdH_2 is estimated at −45 kcal./mole from the unpublished work of R. N. Mulford of this Laboratory on PrH_2 and NdH_1.

[7] G. L. Barthauer and D. W. Pearce, *Ind. Eng. Chem.*, **18**, 479 (1946).

[8] F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).